KY.NT.17 SENSORS AND ACTUATORS: SMART CYRSTALS. R. E. Newnham, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA.

One of the qualities that distinguishes living systems from inanimate matter is the ability to adapt to changes in the environment. Smart materials have the ability to perform both sensing and actuating functions and are, therefore, capable of imitating this rudimentary aspect of life. Four of the most widely used smart materials are piezoelectric $Pb(Zr,Ti)O_3$, electrostrictive $Pb(Mg,Nb)O_3$, magnetostrictive $(Tb,Dy)Fe_2$, and the shape memory alloy NiTi. All four are ferroic with active domain walls, and two phase transformations which help tune the properties of these active materials. $Pb(Zr,Ti)O_3$ is a ferroelectric ceramic which is cubic at high temperature and becomes ferroelectric on cooling through the Curie temperature. At room temperature, it is poised on a rhombohedral-tetragonal phase boundary which enhances the piezoelectric coefficients. Terfenol, $(Tb,Dy)Fe_2$, is also cubic at high temperature and then becomes magnetic on cooling through its Curie temperature. At room temperature, it too, is poised on rhombohedral-tetragonal transition which enhances its magnetostriction coefficients. $Pb(Mg,Nb)O_3$ and Nitinol (NiTi) are also cubic at high temperatures, and on annealing, undergo an order-disorder transformation to a different cubic space group. On further cooling, the partially ordered $Pb(Mg,Nb)O_3$ structure goes through a diffuse phase transformation at room temperature where it exhibits very large dielectric and electrostrictive coefficients. Just below room temperature, it transforms to a ferroelectric rhombohedral phase. The ordered shape memory alloy NiTi undergoes an austenitic (cubic) to martensitic (monoclinic) phase change just above room temperature. It is easily deformed in the martensitic state but recovers its original shape when reheated to austenite. The structural similarities between these four superb actuator materials is remarkable. A review of the applications and structure-property relationships in these and other smart materials will be presented.

KY.NT.18 HELICAL POLYAMIDES AND RINGS: A BRIDGE BETWEEN NYLONS AND PROTEINS. Juan A. Subirana, Dept. Enginyeria Química, Univ. Politécnica de Catalunya, Diagonal 647, E-08028 Barcelona, Spain. e-mail: Subirana@eq.upc.es

In order to bridge the gap between nylons and proteins, synthetic polyamides with a conformation similar to that found in proteins have been studied. Analogies in the folding process are discussed in the last part. We have found that it is possible to obtain structures very similar to the α helix by introducing side chains in nylon 3 and in nylon 4, which is equivalent to introducing one or two methylene groups in the polypeptide main chain. Although the density of intramolecular hydrogen bonds decreases, the helical structure is stable. In some cases, even two different types of helix are found, which crystallize in different structures. In solution it is possible to study the helix-coil transition. The helices may also give rise to liquid crystals and fibers with piezoelectric properties.

In another line of endeavour we have investigated polyamides in which glycine and related monomer units ($-NHCOCH_2$ CONH-; $-CONHCH_2NHCO-$) have been introduced. We find a strong preference of the conformational angles of the glycine units and related monomers to be similar with those found in helical polyglycine II. It is striking that in the presence of glycine fully extended chains, typical in polyamides, are seldom found. These polymers are organized with either one, two or three directions of hydrogen bonding which form new unique structures instead of the familiar extended chains of polyamides and pleated sheets of proteins. Besides the intrinsic interest of these new polymers, our studies open the way to new types of protein engineering based on new monomeric building blocks. We have also used oligomers and rings as model compounds. In some cases, they form hydrogen bonded columns with an appearance similar to the α helix.

With respect to the folding process, many of these polymers form lamellar crystals with 40-80Å thickness, a value which depends on the density of hydrogen bonds. The crystallization process appears to be strongly influenced by the coil-globule transition which takes place in the dilute polymer solution before crystallization. In this way **polymer crystallization appears to have some analogies with the protein folding process.** It is striking that the thickness of polymer lamellae is similar to the common dimensions of proteins.

KY.NT.19 STUDIES ON THE LOADING AND RECOGNITION OF ANTIGENS ON MHC MOLECULES Don C. Wiley, Dept. of Molecular and Cellular Biology, Harvard University and Howard Hughes Medical Institute, Cambridge, Massachusetts, 02138.

In the cellular immune response, antigen specific cell-cell recognition results from the binding of an antigen receptor (TCR) to the complex of an antigenic peptide bound to a class I or class II major histocompatibility complex (MHC) glycoprotein. The TCR is a glycoprotein on the membrane of T lymphocyte and the MHC molecule is on the surface of a target cell. Specific receptor binding triggers signals within T cells that are central to the development of the T-cell repertoire, regulation of the immune response, and activation of cytolytic T cells (CTL). Generalizations about the mechanisms of peptide recognition by class I and class II MHC molecules derived from X-ray crystal structures and biochemical analyses will be reported[1,2,3,4].

The loading of antigenic peptide on class II MHC molecules involves an escort protein called the Invariant chain (Ii). This molecule stabilizes class II molecules and escorts them to a cellular compartment where they bind antigenic peptides. Our NMR and biochemical experiments indicate that Ii may be partially unfolded so that a segment of it can bind into the peptide binding site[5,6]. The X-ray structure of a fragment of this peptide-loading intermediate has been determined by X-ray crystallography[7].

The recognition of peptide/MHC molecule complexes is being studied by assembly of a ternary complex of TCR/peptide/MHC class I molecule. The ectodomains of human TCR class I MHC have been expressed as insoluble inclusion bodies in bacteria and refolded. The antigen specific cell-cell interaction complex has been assembled and shown to retain the binding specificity of the *in vivo* intercellular interaction. This complex has been crystallized[8] and its structure is being determined.

[1]Bouvier, M. and Wiley, D.C., PNAS in press, 1996.
[2]Guo, H-C et al., in preparation.
[3]Stern, L.J. et al., Nature 368, 215-221, 1994.
[4]Jardetzky, T.S. et al., PNAS 93, 734-738, 1996.
[5]Jasanoff, A. et al., PNAS 92, 9900-9904, 1995.
[6]Park, S.-J. et al., PNAS 92, 11289-11293, 1995.
[7]Ghosh, P. et al., Nature 378, 457-462, 1995.
[8]Garboczi et al., in preparation.

KY.NT.20 STRUCTURAL CHEMISTRY OF ORGANIC-INORGANIC MESOPHASES. A. Monnier, C.C. Landry and G.D. Stucky, Dept. of Physical Chemistry, University of Geneva, 30, Q.E. Ansermet, 1211 Geneve 4, Switzerland.

Since the discovery of highly ordered silicates mesoporous materials of the MCM41 family in 1992 (pore size in the range 20-100 A), much effort has been devoted to the study of organic-inorganic supramolecular self-assemblies and their subsequent polymerization, leading to highly structured mesoporous materials. The research in this field is largely fueled by the search of new materials to be used as heterogeneous catalysts, ultraselective molecular sieves, mesoscopically structured hosts, for optically or biologically active guests, or more marginally, as substrates to enter into the realm of mesoscale electronic devices.

Several morphologies, most of which correspond to various phases already known in the water-surfactant lyotropic liquid crystal systems, were synthetised as silicate mesoporous materials. However, a thorough understanding of the various molecular forces acting cooperatively for the formation of organic-inorganic mesophases is crucial in order to improve the quality and increase the variety of the targeted mesoporous materials. This quest represent a research topic on its own, and it is the goal of this talk to present the current status of this topic at both the

experimental and theoretical levels.

The experimental data accumulated to date on the synthesis and characterization of silicates mesoporous materials strongly support the view that a good theoretical model will be most suitably grounded on the aggregation colloids chemistry and on the lyotropic liquid crystal physico-chemistry. Some aspects, specific to the unique ability of silicates to polymerize must also be included to get a coherent picture. A short review of the backgrounds in these fields, with a special emphasis on X-ray diffraction techniques, will be made.

Then, experimental data illustrating the differences and similarities existing between the 'standard' lyotropics liquid crystals and the silicatropic liquid crystals will be presented. This comparison helps to identify the leading forces governing the formation of the silicatropic mesophases and their subsequent polymerization. In turn this allows a model to be presented which is consistent with the behavior of the silicate-surfactant supramolecular assemblies observed so far. The proposed model provides insight into how the various synthesis conditions favor a particular morphology and also suggests possible synthesis modifications to enhance the quality of the final material.

Finally, recent diffraction experiments revealing various phase transitions occurring during the synthesis of the mesoporous material will be presented. The occurrence of these phases transitions will be discussed within the frame of the above proposed model.

As a conclusion, several directions for future investigations will be outlined with their potential consequences for the development of this rapidly growing research field.

KY.NT.21 GROWTH, CHARACTERIZATIONS & APPLICATIONS OF DIAMOND FILMS. Pieter Bennema

KY.NT.22 PROTEIN STRUCTURES: THEIR VALIDATION FOLD CLASSIFICATION AND INTERACTIONS. Janet M. Thornton[1,2], E.G. Hutchinson[1], S. Jones[1], R.A. Laskowski[1,2], M. W. MacArthur[1], A. Michie[1] and C.M. Orengo[1], [1]Department of Biochemistry and Molecular Biology, University College, Gower Street, London WC1E 6BT, [2] Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX

As the number of known protein structures rises rapidly, we begin to appreciate the extent of the universe of protein folds. For each new structure apart from its unique biological interest, it is essential to validate the co-ordinates, to describe the structure in terms of its relationship to other known structures and their functions, and to study the interactions made by the protein with other biomolecules. Since structures are often solved very rapidly it has become essential to develop approaches and software tools which facilitate automated validation, analysis and classification of the structure for the crystallographer. These tools are valuable for users of the databank .

In this presentation, three different aspects of structural analysis will be considered. First, methods for validating structures, based on current knowledge derived from known structures will be discussed. These methods complement the critical measure of agreement between the model and X-ray data. Recent results derived from very high resolution structures will be presented. Secondly, as the size of the database grows it becomes more difficult to know whether a structure is novel or has been seen before. Our hierarchical description of protein structure in terms of Class, Architecture, topology and homologous superfamily (CATH) will be described. Lastly, novel approaches to identifying active sites and recognition patches on the surface of a protein will be discussed.

Information available at http://www.biochem.ucl.ac.uk/bsm

KY.NT.23 DIRECT METHODS IN REAL AND RECIPROCAL SPACE. George M. Sheldrick, Universität Göttingen, Germany

Conventional direct methods that use probability relations to determine the phases of a limited number of reflections are computationally extremely efficient for small structures, but the chances of success decrease sharply as the number of independent atoms increases above about 200. They also require fairly complete data to atomic resolution. It appears that the size barrier has at last been broken by methods that iterate between real and reciprocal space, pioneered by the 'Shake and Bake' program developed by the Buffalo group (Miller et al., 1993). Given a powerful enough computer, much larger structures can be solved than were possible with pure reciprocal space direct methods. The success rate can be improved if slightly better than random starting phases are available, e.g. from automated Patterson interpretation (Sheldrick & Gould, 1995). Such a Patterson-based structure expansion enabled the ab initio solution of a small metalloprotein with about 840 non-hydrogen atoms in the asymmetric unit (Frazao et al., 1995). However these methods still require data to atomic resolution, which in practice means about 1.2 Å.

The next breakthrough will probably be the more active use of general structural knowledge in the real-space part of these procedures, rather than simply peak picking; it is possible that this will lead to a relaxation of the atomic resolution requirement. This talk will review recent progress towards the ab initio solution of both small-moiety and macromolecular structures.

C. Frazao, C.M. Soares, M.A. Carrondo, E. Pohl, Z. Dauter, K.S. Wilson, M. Hervas, J.A. Navarro, M.A. De la Rosa & G.M. Sheldrick (1995). *Structure* 3, 1159-1169.

R. Miller, G.T. DeTitta, R. Jones, D.A. Langs, C.M. Weeks & H. Hauptman (1993). *Science* 259, 1430-1433.

G.M. Sheldrick & R.O. Gould (1995). Acta Cryst. B51, 423-431.

KY.NT.24 NEUTRON DIFFRACTION STUDIES OF COORDINATION AND ORGANOMETALLIC COMPOUNDS. Thomas F. Koetzle, Chemistry Department, Brookhaven National Laboratory, P.O. Box 5000, Upton, NY 11973-5000 USA

In the 50 years since Shull and Wollan's pioneering experiments at Oak Ridge National Laboratory, neutron diffraction has been used to attack a wide range of structural problems in inorganic and organometallic chemistry. These studies exploit the unique properties of neutrons that make them a powerful probe and complement to x rays in crystallographic research. Neutrons are highly sensitive to hydrogen and light atoms in general, have the ability to reveal nuclear positions and mean displacements without bias from the effects of the electron distribution, can detect isotopic substitutions, and are sensitive probes of magnetism.

This lecture will concentrate on single-crystal neutron diffraction, and will illustrate the field with examples taken from work at both reactor and spallation neutron sources. Topics discussed will include structures of metal hydrogen compounds, use of deuterium labelling to investigate reaction mechanisms, structures of ice and gas clathrate hydrates, and studies of spin-density distributions in open-shell systems.

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